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DE-A- 3 710 183 FR-A- 1 470 725 DE-A- 3 731 835

FR-A- 2 601 467

GB-A- 2 113 860

US-A- 4 621 040

PATENT ABSTRACTS OF JAPAN vol. 12, no. 113 (M-683)(2960) 09 April 1988, JP-A-62 240586 (SEIKO INSTRUMENTS AND ELEC-TRONICS LIMITED) 21 October 1987,

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### Description

The present invention relates to a method of forming an image with the use of a laser beam and, more particularly, to a method for heat-sensitive recording wherein a laser beam is utilized as a source of heat energy provided at selected regions of a light-absorbing layer and a binder encapsulated in frangible microcapsules.

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A heat-sensitive recording system is well known in which a thermal head is brought into close proximity to the surface of a heat-sensitive recording material comprising a heat-sensitive coloring layer as provided on a support and scanned thereover so as to transfer the heat energy of the thermal head to the heat-sensitive coloring layer directly, or indirectly through an intervening protective layer thereby, so as to record or form a colored image on the heat-sensitive recording material. For instance, this technology has application to facsimiles or printers. However, in such a heat-sensitive recording process where a thermal head is close to a heat-sensitive recording material and is scanned thereover, various problems often are encountered in that a faithful image can not be recorded, or the thermal head is broken since the thermal head is abraded and worn, or the constituents of the heat-sensitive recording material adheres to the surface of the thermal head. Additionally, in the above heat-sensitive recording system using a thermal head, high-speed control in heating and cooling the heating element or elevation of the heating element density is limited because of the structural characteristic of the thermal head itself. Therefore, realization of high-speed recording or high-density and high-quality recording is often difficult in the heat-sensitive recording system

On the other hand, in order to overcome the above-mentioned problems in a heat-sensitive recording system using a thermal head, employment of a laser beam to effect high-speed and high-density heat-recording without the need for contact between the energy source and the heat-sensitive recording material has been proposed.

One of the proposed techniques is to directly irradiate a heat-sensitive coloring layer with a laser beam to form an image thereon. In general, since the heat-sensitive coloring layer could hardly absorb visible rays and infrared rays, the technical matters relating to how the laser could be absorbed efficiently by the heat-sensitive coloring layer and to how the absorbed heat energy could be utilized efficiently in the coloring reaction are important themes addressed in the technical development of the image-forming process technology. For instance, various techniques concerning the image-forming process have been described in JP-A-50-

23617, JP-A-54-121140, JP-A-57-11090, JP-A-58-56890, JP-A-58-94494, JP-A-58-134791 (corresponding to U.S. Patent 4,510,512), JP-A-58-145493 (corresponding to U.S. Patent 4,510,512), JP-A-59-89192 (corresponding to U.S. Patent 4,529,992), JP-A-60-205182 and JP-A-62-56195 and WO- 8607312A. (The term "JP-A" as used herein means an unexamined published Japanese patent application.) However, in carrying out these illustrated proposals, heat energy necessary for coloration could be obtained only where the output power of the laser is relatively high in magnitude. As a result, it was extremely difficult to prepare a compact and inexpensive apparatus for carrying out the proposed methods. In addition, since the laser ray-absorbing substance to be contained in the heat-sensitive coloring layer is colored in accordance with the illustrated proposals, there is still another problem that the image to be recorded is a low-contrast and low-quality one. In general, most light-absorbing substances are inorganic compounds. However, almost all of them have lightabsorbing efficiency. On the other hand, organic compounds which have a high light-absorbing efficiency and which have softer colors have not yet been devised.

On the other hand, as still another proposal for overcoming the above-mentioned problems in the prior art heat sensitive recording system methods, WO-8804237-A has proposed a means of separating a laser ray-absorbing layer from an imageforming layer. In accordance with this proposal, carbon black, which is recognized to have a good laser ray-absorbing efficiency, is employed whereby the efficiency of absorbing the laser ray is elevated, and the irradiated carbon black is transferred onto the synthetic polymer film as fused because of the generated heat. That is, carbon black serves as both the light-absorbing substance and the image-forming substance in this method. However, this has the disadvantage that a large amount of heat energy is required for fusing the synthetic polymer film, and, therefore, a low-power laser is ineffective in practicing this method.

US-A-4621040 discloses a method of image-forming by imagewise irradiating with a laser a recording material having (a) layer of microcapsules, inert to the laser, containing an ink (solution or suspension of a pigment or dye), and (b) a laser-absorbtive barrier layer which prevents migration of the ink, superposing an image-receiving layer and rupturing the microcapsules, e.g. by pressure rollers, so that the ink in the exposed areas diffuses through the barrier layer, which has been rendered permeable where irradiated, onto the receiving layer.

JP-A-62-240586 disclosed a method using a material having a mixture of microcapsules contain-

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ing colorants, irradiating with laser beams of different wavelengths, so that the colorants are used to form latent images, and rupturing the capsules by pressure to discharge from the uncured microcapsules leuco dyes which react with couplers in a receiving sheet to form colored images.

DE-A-3710183 (= EP-0338025) describes the use of a laser device for transfer printing, using an ink ribbon having, on a carrier film transparent to the laser, microcapsules which are broken by the laser and contain printing inks; by pressure means the inks are transferred imagewise to a paper image receptor. The inks may be absorbent of selected laser radiation.

As mentioned above, various high-speed and high-density heat-sensitive recording materials which may be heat-recorded by use of a laser beam without the need for contact between the material to be recorded and the energy source have heretofore been proposed. However, an image-recording system capable of being effected by the use of a low-power laser has not been devised.

The object of the present invention is to overcome the aforesaid problems and to provide an image-forming method in which an image having a rich gradation, reproducibility and a high contrast can be formed by a high-speed and high-density recording system using a low-power laser.

The important factor for constructing a heatsensitive recording system involving conversion of the light energy generated by a laser beam source into heat energy, and utilizing the thus converted light-to-heat energy comprises selection of a suitable light-absorbing substance, selection of the suitable means of utilizing the heat energy and suitable stabilization of the image as recorded.

However, in the prior art technique as illustrated in the above-mentioned WO-8804237-A, the heat energy required to stably transfer the image is inordinately high, and this is inconsistent with the object of the present invention, i.e., providing low-power laser usage, and a solution of the problem of high power laser demands is the most important aspect of development of this technology.

The present invention is based on the discovery that stabilization of an image as transferred onto a paper support or synthetic polymer film (image-receiving sheet) can be attained fully by simultaneous transfer of both a light-absorbing substance as an image-forming substance and a binder for fixing the light-absorbing substance on the image-receiving sheet; and the light-absorbing substance and the image-forming substance are most preferably the same compound, for effective utilization of the heat energy.

According to the present invention we provide a method of forming an image comprising: irradiating a heat-sensitive recording material with a laser

beam, wherein said heat-sensitive recording material includes a support having provided thereon a light-absorbing layer containing microcapsules which encapsulate a core substance containing at least a light-absorbing substance and a binder capable of fixing the light-absorbing substance on an image receiving film, so that the irradiated microcapsules are selectively heated by the laser to above their glass transition point and are rendered more easily broken under pressure; and transferring a latent image thus formed on the light-absorbing layer, in accordance with a pattern and amount of laser beam irradiation, to the image-receiving film under pressure thereby to obtain on said image-receiving film a visible image formed of or by the light-absorbing substance and the binder.

To make the recording material, a light-absorbing substance and a binder are first formed into a liquid blend having a high viscosity and thereafter encapsulated into microcapsules, and the microcapsules are then selectively heated by laser irradiation, and the thus heated microcapsules are passed through pressure rollers to rupture their walls to thereby fix the light-absorbing substance and the binder onto the adjacent image-receiving sheet. (While the previous coating of the binder on the image-receiving sheet for the purpose of fixing the light-absorbing substance on the image-receiving sheet could be considered as an alternative method, this, however, would require a superfluous heat energy for melting the binder and would be inconsistent with the energy-efficiency aspect of the invention.)

In the image-forming method of the present invention, the transferring efficiency is higher when the time period running from the laser irradiation to image transference under pressure is shortened. The most preferred embodiment of the present invention is to irradiate the light-absorbing sheet with a laser while the sheet is placed against an image-receiving sheet previously applied under pressure. In this embodiment, the image-receiving sheet is a transparent synthetic polymer film and the laser irradiation is preferably applied through the image-receiving sheet.

The support, which is to be coated with a laser ray-absorbing layer to form a light-absorbing sheet for use in the invention, may be either a paper support sheet or a synthetic polymer support, or a laminate composed of such paper and synthetic polymer support.

The kind of carbon black preferably incorporated into the light-absorbing layer is not specifically limited; for instance, any of furnace black, channel black and thermal black can be used.

The carbon black preferably has a mean grain size of  $10^{-7}$  m (100 millimicrons) or less.

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Alternatively, conventional light-absorbing substances can be also used as the light-absorbing substance in suitable combinations, to increase the absorption of the laser beam, such as copper sulfate as described in JP-A-58-94495, cyanine dyes as described in JP-A-58-94494. zenedithiol/nickel complexes as described in JP-A-57-11090, benzenethiol/nickel complexes as described in JP-A-54-121140, inorganic metal salts as described in JP-A-58-145493 (corresponding to U.S Patent 4,510,512), other known metal oxides, hydroxides, silicates, sulfates, carbonates, nitrates, complex compounds, cyanines, polyenes, as well as colored dyes and pigments used in the paper, textile and paint industries as detailedly described, for examples, in Hiroshi Horiguchi, Sousetsu Gosei Seni (General Explanation of Synthetic Dyes), Sankyo Publishing, Japan.

Examples of colored inorganic pigments are chrome yellow, iron oxide pigment, molybdate orange, cadmium red, Prussian blue, zinc sulfate compounds, cadmium sulfide compounds and silicate compounds. Examples of organic pigments are azo dyes such as permanent yellow R, Hansa Yellow R, meta-nitroaniline orange, red toner, autol orange, pigment orange R, benzidine yellow, vulcan fast yellow G, lake red P, pyrazolone red and Lithol Red, phthalocyanine pigments such as Cuphthalocyanine, and anthraquinone pigments such as indanthrene blue and Helio Fast Blue BL. Examples of dyes are safranine, rhodamine, magenta, alizarin red, Rhoduline Red B, chrysoidine, acetamine orange, auramine, quinoline, euchrysine vellow, Fast Light Yellow, stilbene yellow, azo yellow, metanil yellow, Victoria Green, anthraquinone green, Naphthol Green, methylene blue, diazo blue, Naphthol Blue, Fast Blue, Xylene Blue, methyl violet, Bismarck Brown and chrome brown.

Known pigments may be added to the lightabsorbing substance. For instance, one or more kinds of metal grains such as cobalt, iron or nickel grains, and pigments of metal oxides such as TiO<sub>2</sub>, BaO, NiO, Sb<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZnO, CoO, Al<sub>2</sub>O<sub>3</sub>, CuO or MnO and composite blends of metal oxides thereof can be used.

The polymer substance, which is a component of the binder incorporated into the microcapsules in the present invention together with the light-absorbing substance, is not particularly limited. For instance, any of polyolefins, olefin copolymers, styrene resins, styrene-butadiene copolymers, epoxy resins, polyesters, rubbers, polyvinyl pyrrolidones, polyamides, coumarone-indene copolymers, methyl vinyl ethers, maleic anhydride copolymers, polyamides, polyurethanes, polyureas, acrylate polymers, methacrylate polymers, acrylic acid-long chain alkyl methacrylate copolymers, polyvinyl acetates and polyvinyl chlorides can be employed.

These polymer substances can be used alone or as a mixture of two or more thereof. Of the abovementioned binder polymers, especially preferred are acrylate polymers, methacrylate polymers and styrene-butadiene copolymers.

As a solvent for the components of the binder, an oil-soluble solvent can be used. Such an oilsoluble solvent is a high boiling point solvent which can dissolve or swell the above-mentioned polymers and which has a boiling point of 150°C or higher. For examples, it includes phthalates (e.g., diethyl phthalate, dibutyl phthalate), aliphatic dicarboxylates (e.g., diethyl malonate, dimethyl oxalates), phosphates (e.g., tricresyl phosphate, trixylenyl phosphate), citrates (e.g., O-acetyltriethyl citrate, tributyl citrate), benzoates (e.g., butyl benzoate, hexyl benzoate), fatty acid esters (e.g., hexadecyl myristate, dioctyl adipate), alkylnaphthalenes (e.g., methylnaphthalene, dimethylnaphthalene, monoisopropylnaphthalene, diisopropylnaphthalene), alkyldiphenyl ethers (e.g., o-, m-, pmethyldiphenyl ethers), amide compounds of higher fatter acids or aromatic sulfonic acids (e.g., N,Ndimethyllauroamide, N-butylbenzenesulfonamide), trimellitates (e.g., trioctyl trimellitate), diarylalkanes (e.g., dimethylphenylphenylmethane, 1-phenyl-1methyl-phenylethane, 1-dimethylphenyl-1-1-ethylpheny-1-phenylethane, 1phenylethane, isopropylphenyl-2-phenyl-ethane), as well as chlorinated paraffins having from 8 to 30 carbon atoms and having a chlorination degree of from 10 to 40% by weight.

If desired, the above-mentioned high boiling point solvent may be used in the present invention together with any other organic solvent which does not dissolve or swell the above-mentioned polymers and which has a boiling point falling within the range of from 100 to 250 °C. Examples of such a low boiling point solvent are aliphatic saturated hydrocarbons or mixtures consisting essentially of aliphatic saturated hydrocarbons.

The binder for use within the light-absorbing microcapsule is preferably an oily composition containing three components including one of each of the above-mentioned polymer, the low boiling point solvent and the high boiling point solvent.

The weight ratio of the binder and the lightabsorbing substance is preferably within the range of from 50: 1 to 1:10, more preferably 20:1 to 1:1.

The wall material of the microcapsules is not particularly limited. However, the material preferably has a glass-transition point falling within the range of from 80 to 150 °C and forms a wall easily ruptured when the microcapsules are heated under pressure, at a temperature within the said glass-transition point range and is a substance compatible with the image-forming method of the invention. For instance, polyureas, polyurethanes, polyamides

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polyesters and epoxy resins are suitable.

Methods of preparing these microcapsules are described e.g., in US-A-2,800,458 and 3,111,407, and JP-B-3819574, 42-771 and 36-9168. ("JP-B" denotes an examined Japanese patent publication.)

A method of preparing microcapsules is known, in which a microcapsule wall made of a polyurea is formed around a core substance which contains a light-absorbing substance and a binder and which is dispersed in the form of oily drops. Such a known method can be utilized for preparing the microcapsules in the present invention.

As preferred examples, an interfacial polymerization method, internal polymerization method and external polymerization method are representative.

It is known that capsule walls of polyureas may easily be formed by interfacial polymerization reaction of a polyisocyanate such as diisocyanate, triisocyanate, tetraisocyanate or polyisocyanate prepolymer and a polyamine such as a diamine, triamine or tetramine, or a prepolymer containing two or more amino groups, or piperazine or a derivative thereof, together with a polyol in an aqueous solvent, whereupon polyurea microcapsule walls easily may be formed.

On the other hand, composite capsule walls made of polyureas, polyurethanes and polyamides can be formed by the following methods.

For example, polyurea/polyamide composite walls, or polyurethane/polyamide composite walls, can be prepared by an interfacial polymerization method in which a polyisocyanate and an acid chloride as well as a polyamine and a polyol are used and polymerized whereupon the pH value of the emulsion medium of the reaction liquid is adjusted, and, thereafter, the reaction system is heated for polymerization. Polyurea/polyamide composite walls can be prepared by a polymerization method in which a polyisocyanate an acid chloride and a polyamine are used and polymerized whereupon the pH value of the emulsion medium of the reaction liquid is controlled and thereafter the reaction system is heated for polymerization. The deof the method of preparing polyurea/polyamide composite walls are described, for example, in JP-A-58-66948.

The walls of the microcapsules in the present invention can contain, if desired, a charge-adjusting agent such as metal-containing dyes or nigrosines as well as other known additives. Such additives may be incorporated into the microcapsule walls during formation of the walls or thereafter.

Additionally, the surfaces of the capsule walls may be graft-polymerized with vinyl monomers or the like monomers, if desired, for the purpose of adjusting the charging property of the surfaces. Alternatively, polymers of such monomers may

also be attached to the surfaces of the capsule walls for the same purpose.

For coating the microcapsules formed as mentioned above on a support, any known aqueous coating system or organic solvent coating system method can be employed as described, for example, in U.S. Patents 2,681,294, 2,761,791, 3,508,947, 2,941,898 and 3,526,528, and U. Harasaki, Coating Engineering, published by Asakura Shoten (1973). For example, the following compounds may be used with the microcapsules for the purpose of stably and uniformly coating the light-absorbing layer and of enhancing the strength of the coated film, namely, methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, starches, gelatin, polyvinyl alcohol, carboxy-modified polyvinyl alcohol, polyacrylamide, polystyrene copolymers and thereof, polyesters copolymers thereof, polyethylene and copolymers thereof, ероху resins, acrylate methacrylate/resins and copolymers thereof, silicone resins, polypropylene and copolymers thereof, polyurethane resins and polyamide resins. The weight ratio of the above-mentioned additional compound to the carbon black may be from 0.01/1 to 10/1. Additionally, known surfactants may also be employed, if desired, for the purpose of stably blending the microcapsules and the above-mentioned coat film-constituting agents. Examples of surfactants usable for this purpose include anionic surfactants such as alkali metal salts of sulfosuccinic acid or alkali metal salts of polystryrenesulfonic acid; nonionic surfactants, surfactants such as polyoxyethylene alkylethers; and cationic surfactants such as long chain alkyltrimethylammonium salts.

In the recording material it is preferred that the light-absorbing layer is coated so as to have the light-absorbing substance in a coverage of from 0.1 to 10 g/m<sup>2</sup>.

A transparent synthetic polymer film is preferably used as the image-receiving layer. Examples of the film include polyester films such as polyethylene terephthalate film or polybutylene terephthalate film; cellulose derivative films such as cellulose triacetate film; polyolefin films such as polystyrene film, polypropylene film or polyethylene film; as well as polyimide films, polyvinyl chloride films, polyvinylidene chloride films, polyacrylic films, and polycarbonate films. These may be used singly or as laminates composed of two or more thereof. The transparent synthetic polymer film for use in the present invention is preferably one which has a high transparency and does not absorb the laser beam irradiated thereon and which does not deform by heat due to laser irradiation and has a high dimentional stability. The thickness of the film is preferably from 10 μm (microns) to 200 μm

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(microns).

The laser beam which is employed in the present invention may be a type having a wavelength range falling within the visible light region, near-infrared region or infrared region. Examples thereof include a helium-neon laser, an argon laser, a carbon dioxide gas laser, a YAG laser and a semiconductor laser.

In the method of the present invention of irradiating a light-absorbing layer with a laser beam, a latent image is formed in accordance with the irradiated target site pattern and amount. The irradiated latent image is differentiated from the non-irradiated region, since the heat generated by the laser irradiation is imparted to the capsule walls and the capsule walls are thereby heated to a temperature higher than the glass-transition point thereof and become more easily broken or frangible under pressure.

The thus formed latent image is then transferred to a paper or synthetic polymer support under pressure to form a visible image of light-absorbent and binder thereon. Preferably this pressure is imparted to the light-absorbing sheet immediately after the laser irradiation (generally, within several seconds or less after irradiation treatment).

The pressure necessary for transferring the image is from 49 to 490 x  $10^5$  Pa (50 to 500 kg/cm²), preferably from 98 to  $294 \times 10^5$  Pa (100 to 300 kg/cm²). It is preferred that heating is effected simultaneously with application of pressure to the sheet. The heating temperature is, although varied in accordance with the material of the microcapsule walls, preferably a temperature lower than the glass-transition temperature of the wall material polymer by about 10 to  $50 \, ^{\circ}$  C.

In the most preferred embodiment of the image-forming method of the present invention, pressure rollers which have previously been heated to a temperature lower than the glass-transition temperature (Tg) of the microcapsule wall material polymer by 10 to 50°C are used and the lightabsorbing layer of the light-absorbing sheet (recording material) is tightly attached to the imagereceiving sheet made of a transparent synthetic polymer film under pressure of from 98 to 294 x 105 Pa (100 to 300 kg/cm2) with the rollers, whereupon a laser beam is irradiated upon the attached sheets through the image-receiving layer so that the laser beam is focused at the interface between the light-absorbing layer and the image-receiving film, and thereafter the image-receiving sheet is peeled off from the light-absorbing sheet to obtain a recorded image. Thereby a negative image is formed on the image-receiving sheet while a positive image is formed on the light-absorbing sheet. Accordingly, both sheets may be so planned that both images as formed on the two sheets may be utilized, if desired. In this embodiment, not only is the transference efficiency under pressure elevated but also the irradiation energy may be economized since the temperature of the light-absorbing layer is to be already raised prior to laser irradiation.

The following example illustrates the present invention in more detail. The percentages are by weight.

### EXAMPLE

40 g of a solution prepared by blending 1-isopropylphenyl-2-phenylethane containing 50% of polyisobutyl methacrylate (trade name: Acryl Base MM-2002-2, product by Fujikura Chemical Co.) and Isopar-H (aliphatic saturated hydrocarbon mixture, product of Exxon Co.)in a weight ratio of 6/5, and 3 g of an acidic carbon black (trade name: RAVEN 5000, pH 2.8: product of Colombian Carbon Japan Co.) were kneaded and dispersed in an automatic mortar to prepare a dispersion.

Separately, a solution of 20 g of an adduct comprising 3 mols of xylene diisocyanate and one mol of trimethylolpropane (trade name: Takenate D110-N: Product by Takeda Chemical Industry Co.) dissolved in 20 g of ethyl acetate was prepared. The solution was then blended with the abovementioned dispersion to give an oily phase. Preparation of the oily phase liquid blend (blend of core substance and capsule wall material) was effected with adjusting the temperature of the liquid to be 25 °C or lower.

0.2 g of diethylene triamine was added to 200 g of an aqueous 4% solution of methyl cellulose (methoxy group substitution degree: 1.8; mean molecular weight: 15,000) to prepare an aqueous medium, which was then cooled to 15 °C.

The above-mentioned oily phase liquid blend was emulsified and dispersed into the aqueous medium to obtain an oil-in-water emulsion where the oil drops had a mean grain size of about 12  $\mu$ m (microns).

About 10 minutes after preparation of the emulsion, 50 g of an aqueous 2.5% solution of diethylene triamine was gradually and dropwise added to the emulsion, which was then stirred in a thermostatic bath at 60 °C for 3 hours to complete encapsulation.

The thus prepared capsules-containing liquid was coated on a 75  $\mu m$  (micron) thick polyethylene terephthalate film at a solid amount of 1.0 g/m², which was then dried at 50 °C for 30 minutes to obtain a light-absorbing sheet.

The light-absorbing sheet was wound around a heat-roller and heated at 80 °C while being irradiated with a one-msec laser beam (a helium-neon laser) with an energy of 0.1 J/cm². Next (after 0.3 seconds), an image-receiving sheet of 75 µm (mi-

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cron) thick polyethylene terephthalate film was lapped over the light-absorbing sheet around the heat-roller and a pressure of 147 x 10<sup>5</sup> Pa (150 kg/cm<sup>2</sup>) was imparted to the thus lapped sheets. After peeling the image-receiving sheet from the light absorbing sheet, a black transferred image was obtained on the receiving sheet.

15 minutes after the image-transference under pressure, the transferred image was rubbed with the fingers, which resulted in no change in the integrity of the transferred image.

In the same manner, a transferred image was also obtained by irradiation with a 0.5-msec laser. The density of the obtained transferred image portion of each sample was measured with a Macbeth Densitometer to be 1.23 to 0.45, respectively.

## Claims

- 1. A method of forming an image comprising: irradiating a heat-sensitive recording material. with a laser beam, wherein said heat-sensitive recording material includes a support having provided thereon a light-absorbing layer containing microcapsules which encapsulate a core substance containing at least a light-absorbing substance and a binder capable of fixing the light-absorbing substance on an image receiving film, so that the irradiated microcapsules are selectively heated by the laser to above their glass transition point and are rendered more easily broken under pressure; and transferring a latent image thus formed on the light-absorbing layer, in accordance with a pattern and amount of laser beam irradiation, to the image-receiving film under pressure thereby to obtain on said image-receiving film a visible image formed of or by the light-absorbing substance and the binder.
- A method as claimed in Claim 1, wherein the light-absorbing layer is irradiated while said light-absorbing layer is attached to said imagereceiving film.
- A method as claimed in Claim 1 or 2, wherein the light-absorbing substance is carbon black.
- A method as claimed in Claim 3, wherein said carbon black has a mean grain size of from 10<sup>-7</sup> m (100 millimicrons) or less.
- A method as claimed in Claim 3, wherein said carbon black is selected from furnace black, channel black and thermal black.
- A method as claimed in any preceding claim, wherein said light-absorbing substance is coat-

ed at a coverage of 0.1 to 10 g/m<sup>2</sup>.

- A method as claimed in any preceding claim, wherein said support for the light-absorbing layer is comprised of paper, a synthetic polymer or a laminate thereof.
- 8. A method as claimed in any preceding claim, in which the image-receiving film is a transparent synthetic polymer film and the light-absorbing layer is irradiated through the direction of the image-receiving film.
- 9. A method as claimed in any preceding claim, wherein said binder is an oily composition comprising a polymer, a low boiling point solvent incapable of dissolving or swelling binder polymers and a high boiling point solvent capable of dissolving or swelling binder polymers.
- 10. A method as claimed in Claim 9, wherein said binder contains a polymer selected from polyolefins, olefin copolymers, styrene resins, styrene-butadiene copolymers, epoxy resins, polyesters, polyvinyl pyrrolidones, polyamides, coumarone-indene copolymers, methyl vinyl ethers, maleic anhydride copolymers, polyamides, polyurethanes, polyureas, acrylate polymers, methacrylate polymers, acrylic acidlong chain alkyl methacrylate copolymers, polyvinyl acetates and polyvinyl chlorides.
- 11. A method as claimed in any preceding claim, in which the wall materials of the microcapsules is a polyurea, polyurethane, polyamide, polyester or epoxy resin, and it has a glass transition point in the range of from 80 to 150 °C and is rupturable under pressure when heated at a temperature falling within said glass-transition temperature range.
- 12. A method as claimed in any preceding claim, wherein said laser beam is generated from a laser source selected from a helium-neon laser, an argon laser, a carbon dioxide laser, a YAG laser and a semiconductor laser.
- 13. A method as claimed in any preceding claim, wherein said latent image transferring pressure is from 49 to 490 x 10<sup>5</sup> Pa (50 to 500 Kg/cm<sup>2</sup>).
- 14. A method as claimed in any preceding claim, wherein pressure rollers are used which were previously heated to a temperature lower by 10 to 50 °C than the glass-transition temperature of the microcapsule wall material polymer, and the light-absorbing layer is pre-attached to

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the image-receiving film made of a transparent synthetic polymer film under a pressure of from 100 to 300 kg/cm<sup>2</sup> with said rollers, whereafter a laser beam is irradiated upon the attached sheets through the image-receiving layer in a manner such that the laser beam is focused at the interface between the light-absorbing layer and the image-receiving film, and thereafter the image-receiving sheet is peeled off from the light-absorbing sheet to obtain a recorded image.

# **Patentansprüche**

- Verfahren zur Erzeugung eines Bildes, umfassend: Bestrahlen eines wärmeempfindlichen Aufzeichnungsmaterials mit einem Laserstrahl, wobei das wärmeempfindliche Aufzeichnungsmaterial einen Träger einschließt mit einer darauf angeordneten lichtabsorbierenden Schicht, enthaltend Mikrokapseln, welche eine Kernsubstanz einkapseln, die wenigstens eine lichtabsorbierende Substanz und ein zum Fixieren der lichtabsorbierenden Substanz fähiges Bindemittel auf einem bildempfangenden Film enthält, so daß die bestrahlten Mikrokapseln selektiv durch den Laser über ihren Glasübergangspunkt erhitzt werden und leichter unter Druck brechen können; und Übertragen eines so auf der lichtabsorbierenden Schicht erzeugten latenten Bildes in Einklang mit einem Muster und einer Menge der Bestrahlung mit Laserstrahl, auf dem bildempfangenden Film unter Druck, um dabei auf dem bildempfangenden Film ein sichtbares Bild zu erhalten, das durch oder von der lichtabsorbierenden Substanz und dem Bindemittel erzeugt wird.
- Verfahren nach Anspruch 1, worin die lichtabsorbierende Schicht bestrahlt wird während die lichtabsorbierende Schicht auf dem bildempfangenden Film angebracht ist.
- Verfahren nach Anspruch 1 oder 2, worin die lichtabsorbierende Substanz Ruß ist.
- Verfahren nach Anspruch 3, worin der Ruß eine mittlere Korngröße von 10<sup>-7</sup> m (100 Millimikron) oder weniger besitzt.
- Verfahren nach Anspruch 3, worin der Ruß ausgewählt ist aus Ofenruß, Gasruß und thermischem Ruß.
- Verfahren nach einem der vorhergehenden Ansprüche, worin die lichtabsorbierende Substanz mit einem Auftrag von 0,1 bis 10 g/m² beschichtet ist.

- 7. Verfahren nach einem der vorhergehenden Ansprüche, worin der Träger für die lichtabsorbierende Schicht aus Papier, synthetischem Polymer oder einem Laminat davon besteht.
- Verfahren nach einem der vorhergehenden Ansprüche, worin der bildempfangende Film ein transparenter synthetischer Polymerfilm ist und die lichtabsorbierende Schicht durch den bildempfangenden Film hindurch bestrahlt wird.
- Verfahren nach einem der vorhergehenden Ansprüche, worin das Bindemittel eine ölige Zusammensetzung ist, umfassend ein Polymer, ein Lösungsmittel mit niedrigem Siedepunkt, welches nicht fähig ist zum Lösen oder Schwellen von Bindemittel-Polymeren, und ein Lösungsmittel mit hohem Siedepunkt, welches fähig ist zum Lösen oder Schwellen von Bindemittel-Polymeren.
- 10. Verfahren nach Anspruch 9, worin das Bindemittel ein Polymer enthält, ausgewählt aus Polyolefinen, Olefin-Copolymeren, Styrolharzen, Styrolbutadien-Copolymeren, Epoxyharzen, Polyestern, Polyvinylpyrrolidonen, Polyamiden, Methylvinyle-Cumaroninden-Copolymeren, thern, Maleinsäureanhydrid-Copolymeren, Po-Ivamiden. Polyurethanen. Polyharnstoffen, Acrylat-Polymeren, Methacrylat-Polymeren, langekettigen Acrylsäure-Alkylmethacrylat-Copolymeren, Polyvinylacetaten und Polyvinylchloriden.
- 11. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Wandmaterial der Mikrokapseln Polyharnstoff, Polyurethan, Polyamid, Polyester oder Epoxyharz ist und einen Glasübergangspunkt im Bereich von 80 bis 150 °C besitzt und unter Druck zerbrechbar ist, falls es auf eine Temperatur erhitzt wird innerhalb der Glasübergangstemperaturbereich.
- 12. Verfahren nach einem der vorhergehenden Ansprüche, worin der Laserstrahl von einer Laserquelle erzeugt wird, ausgewählt aus einem Helium-Neon-Laser, einem Argon-Laser, einem Kohlendioxid-Laser, einem YAG-Laser und einem Halbleiter-Laser.
- 13. Verfahren nach einem der vorhergehenden Ansprüche, worin der Übertragungsdruck für das latente Bild 49 bis 490 x 105 Pa (50 bis 500 kg/cm²) beträgt.
- 14. Verfahren nach einem der vorhergehenden Ansprüche, worin Druckwalzen verwendet werden, welche zuvor auf eine Temperatur von 10

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bis 50°C weniger als die Glasübergangstemperatur des Wandmaterial-Polymeren für die Mikrokapseln erhitzt wird und die lichtabsorbierende Schicht zuvor angebracht ist auf den bildempfangenden Film, der hergestellt ist aus einem transparenten synthetischen Polymerfilm unter einem Druck von 100 bis 300 kg/cm² mit den Walzen, wonach ein Laserstrahl auf die angebrachten Blätter durch die bildempfangende Schicht auf eine Weise gerichtet wird, daß der Laserstrahl an der Grenzfläche zwischen der lichtabsorbierenden Schicht und dem bildempfangenden Film fokussiert wird und anschließend das bildempfangende Blatt von dem lichtabsorbierenden Blatt zum Erhalt eines aufgezeichneten Bildes abgeschält wird.

#### Revendications

- Procédé de formation d'une image comprenant: l'irradiation d'un matériau d'enregistrement thermosensible avec un rayon laser, dans lequel ledit matériau d'enregistrement thermosensible comporte un support sur lequel est prévue une couche absorbant la lumière contenant des microcapsules qui enrobent une substance centrale contenant au moins une substance absorbant la lumière et un liant capable de fixer la substance absorbant la lumière sur une pellicule recevant l'image, de telle sorte que les microcapsules irradiées sont sélectivement chauffées par le laser au-dessus de leur point de transition vitreuse et se brisent plus facilement sous pression; et le transfert d'une image latente ainsi formée sur la couche absorbant la lumière, conformément à un modèle et à la quantité d'irradiation par le rayon laser, à la pellicule recevant l'image sous pression, pour obtenir ainsi sur ladite pellicule recevant l'image une image visible formée de ou par la substance absorbant la lumière et le liant.
- Procédé selon Revendication 1 dans lequel la couche absorbant la lumière est irradiée pendant que ladite couche absorbant la lumière est fixée à ladite pellicule recevant l'image.
- Procédé selon Revendication 1 ou 2 dans lequel ladite substance absorbant la lumière est du noir de carbone.
- Procédé selon Revendication 3 dans lequel ledit noir de carbone a une granulométrie moyenne de 10<sup>-7</sup> m (100 millimicrons) ou moins.

- Procédé selon Revendication 3 dans lequel ledit noir de carbone est choisi entre le noir au four, le noir au tunnel et le noir thermique.
- 6. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite substance absorbant la lumière est revêtue à raison de 0,1 à 10 g/m².
- 7. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit support pour la couche absorbant la lumière est constituée de papier, d'un polymère synthétique ou d'un laminé de ces matières.
- 8. Procédé selon l'une quelconque des revendications précédentes, dans lequel la pellicule recevant l'image est une pellicule polymère synthétique transparente et la couche absorbant la lumière est irradiée par la direction de la pellicule recevant l'image.
- 9. Procédé selon l'une quelconque des revendications précédentes dans lequel ledit liant est une composition huileuse comprenant un polymère, un solvant à point d'ébullition bas incapable de dissoudre ou de faire gonfler les polymères du liant, et un solvant à point d'ébullition élevé capable de dissoudre ou de faire gonfler les polymères du liant.
- 10. Procédé selon Revendication 9, dans lequel ledit liant contient un polymère choisi parmi les polyoléfines, les copolymères d'oléfines, les résines de styrène, les copolymères styrène-butadiène, les résines époxides, les polyesters, les pyrrolidones de polyvinyle, les polyamides, les copolymères coumarone-indène, les esters de méthylevinyle, les copolymères anhydrides maléiques, les polyamides, les polyuréthannes, les polyurées, les polymères d'acrylate, les polymères de méthacrylate, les copolymères de méthacrylate, les copolymères de méthacrylate d'alkyle à chaîne longue d'acide acrylique, les acétates de polyvinyle et les chlorures de polyvinyle.
- 11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le matériau de paroi des microcapsules est une polyurée, un polyuréthanne, un polyamide, un polyester ou une résine époxyde, et a un point de transition vitreuse dans la gamme de 80 à 150 °C, et peut être rompu sous pression lorsqu'il est chauffé à une température comprise dans ladite gamme de températures de transition vitreuse.

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- 12. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit rayon laser est produit par une source laser sélectionnée entre un laser à l'hélium-néon, un laser à l'argon, un laser à l'anhydride carbonique, un laser YAG et un laser à semi-conducteur.
- 13. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite pression de transfert d'image latente est comprise entre 49 et 490 x 10<sup>5</sup> Pa (50 à 500 kg/cm<sup>2</sup>).
- 14. Procédé selon l'une quelconque des revendications précédentes, dans lequel sont utiliss des galets de pression qui ont été préalablement chauffés à une température inférieure de 10 à 50°C à la température de transition vitreuse du polymère du matériau de paroi des microcapsules, et où la couche absorbant la lumière est pré-fixée à la pellicule recevant l'image constituée d'une pellicule de polymère synthétique transparent sous une pression de 100 à 300 kg/cm<sup>2</sup> avec lesdits rouleaux, après quoi les feuilles fixées sont irradiées par un rayon laser à travers la couche recevant l'image d'une manière telle que le rayon laser est concentré sur l'interface entre la couche absorbant la lumière et la pellicule recevant l'image, et après quoi la feuille recevant l'image est décollée de la feuille absorbant l'image pour donner une image enregistrée.